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COMBUSTION REGIME SYNTHESIS OF NICKEL-CONTAINING SPINEL-TYPE PIGMENTS

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The results of experimental studies of self-propagating high-temperature synthesis (SHS method) of blue-green nickel-containing spinels are presented. The composition of the compounds is confirmed by IR spectroscopy, x-ray phase analysis, metallographic analysis, and x-ray spectral microanalysis. The effect of the batch composition on the structure and phase compositions of the compounds obtained is shown. The SHS method makes it possible to obtain spinels that could find applications as high-temperature ceramic pigments.

High-temperature pigments have found wide applications in the ceramic industry in the manufacture of ceramics for house wares and art ceramics. Such pigments are of the spinel type. Together with conventional methods for producing such pigments, investigators are becoming increasingly interested in the method of self-propagating high-temperature synthesis (SHS). This method is based on the use of the internal chemical energy of the initial reagents and is an example of an energetically advantageous organization of the synthesis process. The technological processes developed on the basis of the SHS method differ fundamentally from other methods of synthesis by the extreme conditions in the combustion wave. The main advantages of SHS are the equipment simplicity, ecological cleanliness of the process, high temperatures and short duration of the synthesis process, and very low energy consumption [1].

The objective of the present work is to obtain green and blue-green spinel-type nickel-containing pigments by the SHS method and to study the effect of the initial composition on the phase and structure formation processes.

The metal oxides Al_2O_3, Ni_2O_3, Co_2O_3, Co_3O_4, Cr_2O_3, ZnO, and MgO and ASD-4 aluminum powder were used as the initial materials. MPF-3 magnesium served as an energy-carrying additive. Synthesis was conducted in a constant-pressure apparatus. The charge was heated to 800°C. A nichrome coil was used to initiate combustion.

An optical microscope (Unimet, Axiovert 200M) and a scanning electron microscopy (Camebax) were used to investigate the microstructure of the samples obtained. In addition, we performed x-ray spectral microanalysis with the electron microscope. A SDT Q-600 thermal analyzer was used to study the thermal oxidation of the substances in the temperature range 25 – 1500°C with heating rate 10 K/min. The maximum interaction temperature was measured with a tungsten – rhenium thermocouple. The pigments obtained were identified by x-ray phase analysis with a DRON-UM1 diffractometer (CoK_α radiation) and infrared spectroscopy in the range 4000 – 400 cm^{-1} with a Nicolet 5700 IR-Fourier spectrometer[2] with a KBr diffuse-reflection attachment.

In the course of this work, spinel-type pigments in the systems $NiO – Cr_2O_3 – Al_2O_3$, $ZnO – NiO – Cr_2O_3 – Al_2O_3$, $MgO – NiO – Cr_2O_3 – Al_2O_3$, $ZnO – MgO – NiO – Cr_2O_3 – Al_2O_3$, and $NiO – CoO – Cr_2O_3 – Al_2O_3$ were synthesized in a finely disperse state. The synthesis time was several minutes taking account of the heating time, and high temperatures were reached (Fig. 1).

It is known that aluminum-nickel spinel forms at a higher temperature (approximately 1700°C) than aluminum-cobalt spinel. SHS in the system $NiO – Al_2O_3$ did not lead to the formation of spinel. According to IR spectroscopy, corundum forms in the synthesis process; the absorption bands of corundum appear at 746.3, 627.2, 559.6, 470.6, and 427.5 cm^{-1} (Fig. 2, curve *1*) [2 – 4]. X-ray phase analysis showed that nickel oxide and metallic nickel are present in the products of synthesis. Small quantities of the inter-

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[2] Equipment provided by the Scientific and Analytical Center of Tomsk Polytechnical University was used for the IR spectroscopic investigations.

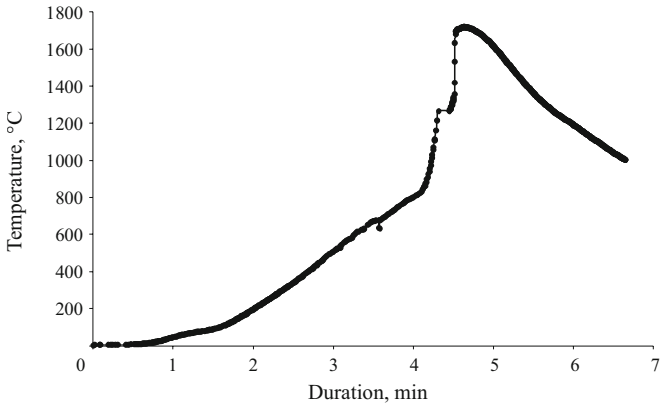

Fig. 1. Thermogram of SHS of a mixture of Al_2O_3, Ni_2o_3, Al, ZnO and Cr_2O_3 nickel-containing pigment.

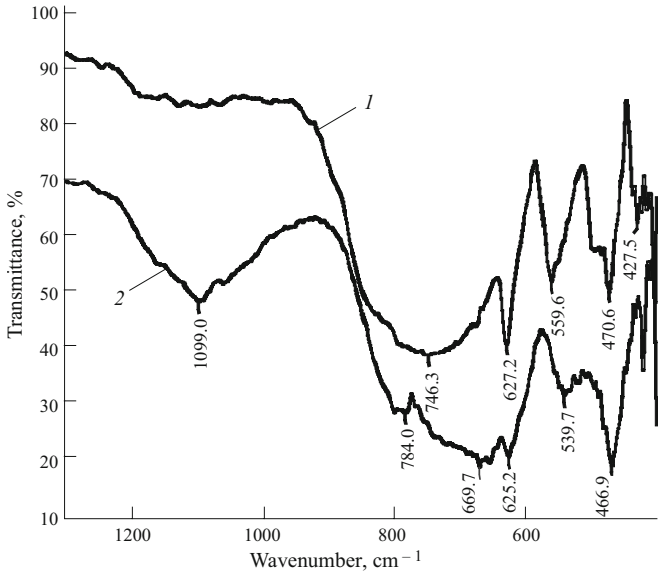

Fig. 2. IR spectra of pigments: *1*) pigment of the system NiO – Al_2O_3; *2*) pigment of the system NiO – Al_2O_3 (excess Al).

metallide Ni_5Al_3 and the high-alumina phase $NiAl_{26}O_{40}$ as well as aluminum nitride AlN are observed.

Increasing the thermicity of the composition by increasing the content of metallic aluminum does not lead to the formation of pure spinel $NiAl_2O_4$ in the product. An inverted spinel is present together with the normal spinel. Vibrations of tetrahedral nickel [NiO_4] manifest at 669.7 cm^{-1}, octahedral aluminum [AlO_6] at 539.7 cm^{-1}, and tetrahedral aluminum [AlO_4] are 784.0 cm^{-1}. In addition, a corundum phase is also present. Absorption bands characteristic for the $(AlO_2)^-$ ion are observed at 1099 cm^{-1} (Fig. 2, curve *2*). The color of the pigment is grey. When the nickel oxide content increases together with that of metallic aluminum, aluminum-nickel spinel in the form of a dense ingot forms.

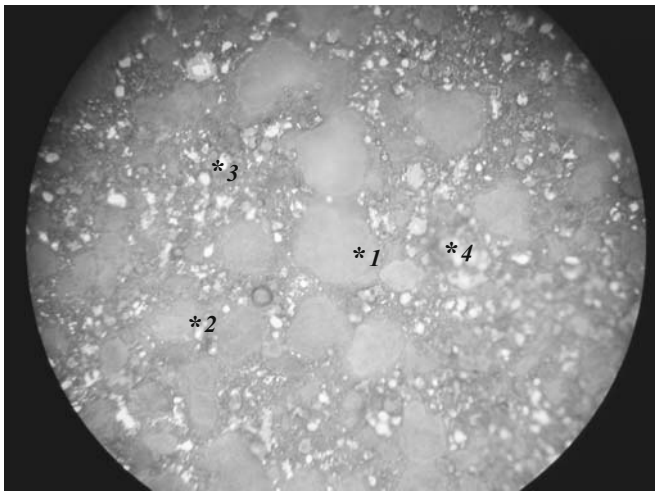

Fig. 3. Microstructure of the nickel-containing pigment in the system ZnO – NiO – Cr_2O_3 – Al_2O_3 (× 200, Axiovert 200M): *1*) Al_2O_3; *2*) $Zn_{1-x}Ni_xAl_2O_4$; *3*) Ni; *4*) $Zn_{1-x}Ni_xCr_2O_4$.

Modifying additives were introduced to obtain finely disperse pigments with good color characteristics. $Mg(NO_3)_2 \cdot 6H_2O$ was used as an oxidizer. ZnO, MgO, and Cr_2O_3 were added to improve the color tone and expand the color palette of the pigments. These compounds resulted in the formation of zinc, magnesium, and chromium spinelides, and they decreased the amount of free Al_2O_3 in the system. The synthesized pigments were green.

Figure 3 shows the microstructure of the nickel-containing pigment. Chromium oxide, which is present in the pigment charge, increases the intensity of the processes which occur by forming zinc and nickel chromium spinels with the composition $Mg_xZn_yNi_{(1-x-y)}Cr_2O_4$. Evidently, the chromium spinels which are formed interact with Al_2O_3 particles and solid solutions of zinc and nickel aluminum spinels $Zn_{1-x}Ni_xAl_2O_4$ are formed on the particle surfaces, thereby destroying the surface of aluminum oxide. All this is confirmed by x-ray spectral microanalysis.

Integrated thermal analysis of the nickel-containing pigment, whose charge consists of a mixture of Al_2O_3, Cr_2O_3, Ni_2O_3, and Al, shows that synthesis proceeds through two Al oxidation stages: an aluminum thermal reaction (900.6°C) and direct oxidation (972.0°C). Synthesis of the chromium and aluminum spinels with Cr_2O_3 starts at 1150°C. Next, a very small mass increase is observed at 1267.4°C. This mass increase is probably due to the oxidation of nickel released during synthesis.

Partial substitution of CoO for NiO also results in the formation of a cobalt spinel. As a result, the pigment acquires a blue-green color.

All pigments obtained by SHS are finely disperse. They pass through a No. 060 sieve and do not require milling. Sieving the pigments showed that the main fraction is comprised of spinel particles less than 50 μm in size.

In summary, ZnO and MgO improve the color tone of the pigments. The introduction of oxidizers into the initial charge facilitates more complete transformation. Chromium-containing additives increase the intensity of the processes that occur. Spinels based on Ni_2O_3 and Al_2O_3 with Cr_2O_3, Co_2O_3, Co_3O_4, ZnO, and MgO as additives form solid solutions in the blue-green range which are heat resistant and can be used for over- and under-glaze colorants.

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